CATALYTIC CRYSTALLIZATION OF ICES BY SMALL SILICATE SMOKES AT TEMPERATURES LESS THAN 20K; M. Moore, R. Ferrante [1], R. Hudson[2], T. Tanabe [3] and J. Nuth, Astrochemistry Branch, Code 691, NASA Goddard Space Flight Center, Greenbelt, MD 20771

Samples of methanol and water ices condensed from the vapor onto aluminum substrates at low temperatures (below ~80 K) form amorphous ices; annealing at temperatures in excess of 140-155K is usually required to convert such amorphous samples to crystalline ices. However, we have found that when either methanol or water vapor is deposited onto aluminum substrates that have been coated with a thin (0.1-0.5 mm) layer of amorphous silicate smoke, the ices condense in crystalline form. We believe that crystalline ice forms as the result of energy liberated at the ice/silicate interface perhaps due to weak bonding of the ice at defect sites on the grains and the very high surface to volume ratio and defect density of these smokes. Annealing of amorphous water ice mixed with more volatile components such as methane, carbon monoxide, etc., has been suggested as an efficient way to produce clatherates in the outer solar nebula and thus explain the volatile content of comets and icy satellites of the outer planets (Lunine et al., 1991). This hypothesis may need to be re-examined if amorphous ice does not form on cold silicate grains.

Silicate smokes were prepared in a bell jar by the evaporation of SiO solid heated in an alumina crucible at T > 1500K followed by vapor phase nucleation and growth in a 100 torr hydrogen atmosphere at the ambient temperatures above the crucible (Nuth and Donn, 1983). Smokes were collected onto aluminum substrates placed from 10-30 cm away from the crucible. This provided considerable variation in the thickness of the smoke layers from relatively thick deposits (> 1mm) to less than a full monolayer of smoke. Smoke-covered substrates were transferred in air from the bell jar to a dessicator where they were stored until needed. Inidividual substrates were attached to a cold finger, evacuated to 10^{-6} torr, cooled to T ~10K then exposed to condensible vapor sprayed onto the surface through a capillary tube from a 5 liter reservoir. The temperature of the substrate was maintained below 15K during deposition of the ice layer (Nuth and Moore, 1989).

Infrared spectra of the ice deposits were obtained using a Mattson Polaris FTIR; the sample beam is reflected from the aluminum substrate resulting in an absorbance spectrum representing two passes through the sample. In studies of the effects of the silicate smoke on the ice, the "background" spectrum used was the initial smoke-covered substrate. In studies of the effect of the ice on the smoke, the reference spectrum used was a polished aluminum substrate free from smoke. Spectra of the ices on the smoke covered substrate were obtained in both the mid-(4000-400 cm^{-1}) and far-(500-100 cm^{-1}) infrared regions in separate experiments due to the need for different beamsplitter/detector combinations to operate in these wavelength ranges. Spectra detailing the changes in the smokes resulting from exposure to the ice were only obtained in the mid-infrared. In both sets of experiments some studies of the effects of irradiating the samples with 1 MeV protons to a total flux of up to 10^{15} protons/cm^2 were undertaken using the GSFC Van der Graaf accelerator.

In general changes in the structure of the silicate smoke due to exposure to water vapor or oxygen, as evidenced by changes in the infrared spectra of the samples, occurred on a relatively long timescale and were usually quite subtle in nature. Larger changes were observed only when water-ice coated samples were annealed at temperatures significantly above 100K or after proton irradiation. More detailed results of these

experiments will be reported elsewhere. Because of the relative stability of the silicate smoke at low temperatures, one smoke-coated subtrate could be used for many volatile-ice studies.

As noted above when either methanol or water vapor was deposited onto a smoke-coated substrate at T <15K, the resultant ice spectra appear to be typical of crystalline ices in both the mid- and far-IR experiments. Ammonia deposited onto the silica coated substrate exhibited a far-IR spectrum intermediate between an amorphous (peak near 417 cm^{-1}) and crystalline (peak near 352 cm^{-1}) ice with maximum absorbance near 388 cm^{-1}. An experiment in which water-vapor was deposited onto a thick (>1 mm) smoke-covered substrate which had remained in the dissicator for ~ 1 month prior to use resulted in an amorphous ice deposit. Because the smoke is a relatively good insulator we might have initially expected this substrate to form a stratified amorphous-crystalline desposit with the amorphous ice near the cold substrate and the more crystalline ice near the outer surface of the smoke. Alternatively we would have expected a crystalline ice deposit. However, production of an amorphous ice can really only be explained if the smoke catalyst had been poisoned by long exposure to air prior to the experiment. This idea leads naturally to the conclusion that the catalytic crystallization occurs via reaction of the vapor with oxygen-defect sites in the solid smoke. In support of this hypothesis we note that deposition of methanol onto silicate smoke results in several bands not observed when methanol is deposited directly onto aluminum. We postulate that these bands represent methanol bonded to oxygen defect sites in the smoke.

Irradiation of crystalline methanol ice on a smoke-covered aluminum substrate results in an amorphous methanol ice and the synthesis of new species such as carbon monoxide and formaldehyde. No substantial changes were noted between irradiation of methanol on silica and similar experiments on an aluminum substrate. Finally, deposition of water or methanol onto silica smoke appears to result in a large decrease in the strength of the far-IR absorbance of the ice. More experiments on the effect of the silica substrate on the far-IR cross-section of water and methanol ices and on the synthesis of new species during the irradiation of methanol ice are needed before firm conclusions can be reached. Experiments to test the hypothesis that active, oxygen-defect sites are responsible for the catalytic production of crystalline ices are also needed. If this hypothesis is correct then follow-up experiments to determine the rate at which such defects are eliminated by exposure to air and water vapor as a function of temperature and partial pressure of the reactive species will also be needed in order to assess the longevity of such catalytic agents in the primordial solar nebula.

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